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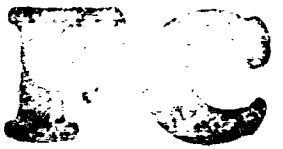
HEAT RESISTANT EXPLOSIVES III 1, 3 — DIAMINO – 2, 4, 6 – TRINITROBENZENE, DATB, FROM 1, 3 — DIMETHOXYBENZENE (C)



15 DECEMBER 1958

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

HEAT RESISTANT EXPLOSIVES III
1,3-DIAMINO-2,4,6-TRINITROBENZENE, DATB, FROM 1,3-DIMETHOXYBENZENE

Prepared by:

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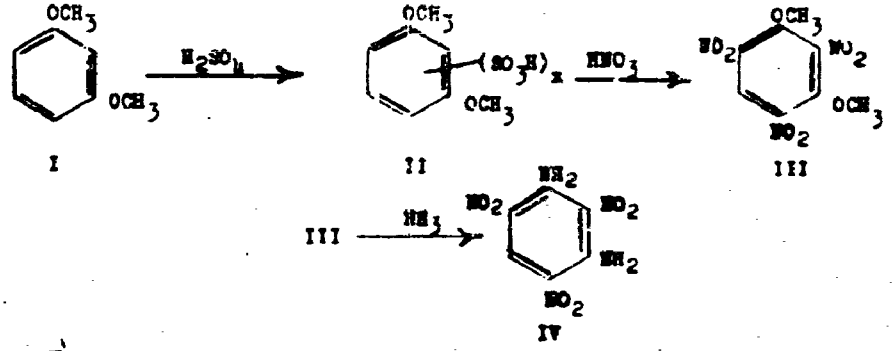
Chief, Organic Chemistry Division

ABSTRACT: A facile method for the preparation of 1,3-diamino-2,4,6-trinitrobenzene, IV, from commercially available 1,3-dimethoxybenzene, I, is described. The method gives yields of 147 parts of IV per 100 parts of I and is easily adaptable to commercial scale production.

Commercial grade I is sulfonated to what is probably a mixture of sulfonic acids, II, and the mixture is then nitrated without isolation to 1,3-dimethoxy-2,4,6-trinitrobenzene, III, at low temperatures. The treatment of III with methanolic ammonia or solutions of ammonium acetate yields IV in a high degree of purity.



Several experimental procedures for the prepartion of large particle size IV are described.

Chemistry Research Department
U. S. NAVAL ORDNANCE LABORATORY
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NAVORD Report 6208 15 December 1958

This report describes a new synthesis of 1,3-diamino-2,4,6-trinitrobenzene from 1,3-dimethoxybenzene. Results indicate that the procedure can be readily adapted to plant scale production. This work was performed under Task No. FR-44, Chemistry of High Energy Compounds.

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Captain, USN
Commander

ALBERT LIGHTBODY
By direction

TABLE OF CONTENTS

ILLUSTRATIONS

HEAT RESISTANT EXPLOSIVES III
1,3-DIAMINO-2,4,6-TRINITROBENZENE, DATB, FROM 1,3-DIMETHOXYBENZENE

INTRODUCTION

Preliminary small scale tests indicated that, as had been predicted in these laboratories, 1,3-diamino-2,4,6-trinitrobenzene (DATB) might well meet the requirements for a heat-resistant insensitive explosive. This prompted the Organic Chemistry Division to undertake the development of methods suitable for the production of this explosive in quantities sufficient for large scale tests.

A method developed by Shipp and Hill (1a) involved the nitration of m-nitroaniline to 2,3,4,6-tetranitroaniline followed by the amination of this compound to DATB. The method was somewhat time-consuming and increased demands for DATB for large scale testing programs made it difficult for the NOL pilot plant to supply sufficient quantities by this route. Efforts were therefore initiated to improve the existing procedure and to find new routes by which this material could be manufactured in large quantities. Kaplan (1b) has accomplished the former objective with the development of an elegant and facile continuous process for the m-nitroaniline nitration; the present report describes a successful effort to meet the latter requirement. The net result of the overall program has been the development in these laboratories of three distinct procedures for the manufacture of DATB, each of which is believed to represent substantial improvement over the best previous method, the conversion of styphnic acid to dichlorotrinitrobenzene then to DATB as reported by Haas, Feuer and Harban (1c).

DISCUSSION

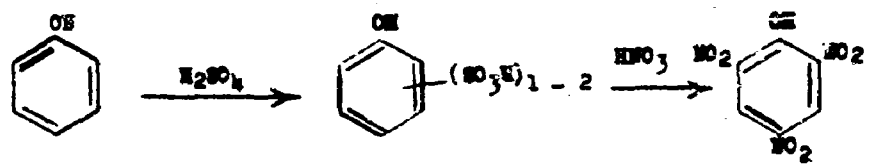
Since it has been demonstrated that tetranitroaniline could be converted to 2,4,6-trinitro-3-methoxyaniline which, in turn, could be aminated to DATB (1a), it seemed reasonable that 1,3-dimethoxy-2,4,6-trinitrobenzene could be aminated by similar procedures. The problem evolved into one of finding a suitable method for the preparation of the dimethoxytrinitrobenzene. The synthesis of this compound from 2,4-dinitroresorcinol by methylation followed by nitration had been reported by Vermeulen (2) in 1919. This procedure seemed too involved and the direct

nitration of m-dimethoxybenzene, available in large quantities from the Koppers Company at about $1.70/lb., was considered as more feasible.

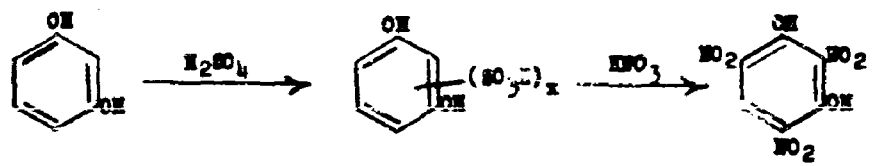
In the first conditions tried, the dimethoxybenzene was allowed to stand in a mixture of 96% nitric acid and acetic anhydride for twenty five hours at room temperature. The product obtained in 82% yield was 1,5-dimethoxy-2,4-dinitrobenzene. Dubinin (3) has reported the same compound as resulting from the treatment of 1,5-dimethoxy-2-nitro-4-tert-butylbenzene with nitric acid in acetic anhydride as have Carpenter, Easter and Wood (4) from the treatment of 1,5-dimethoxy-2,4-di-tert-butylbenzene with nitric acid in a mixture of acetic acid and acetic anhydride.

Due to the similarities between phenol, resorcinol and 1,3-dimethoxybenzene, methods used in the preparation of picric and styphnic acids were next considered. Since the methoxyl group exerts an activating effect towards electrophylic attack at the ortho and para positions, and since its effect is about as great as that of the hydroxyl group, it was surmised that the nitration of 1,3-dimethoxybenzene would be rapid and that low temperatures would suffice. This seemed especially likely since in this compound the 2-, 4- and 6-positions are doubly activated, and it was, indeed, found to be the case.

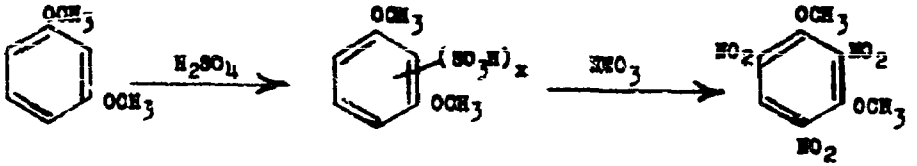
Picric acid is made from phenol (5,6,7) in 75-90% yield by the treatment of its sulfonation products with nitric acid. The process requires approximately twenty-four hours for large scale runs.



Borsche and Feske (8) prepared styphnic acid from resorcinol in 90% yield using a similar procedure.



Modifications of this procedure proved to be very satisfactory in the preparation of 1,3-dimethoxy-2,4,6-trinitrobenzene.



Small scale runs using 10.5 g of the dimethoxybenzene required approximately one hour for completion and gave yields of 87%. The products were of good quality, usually melting at 121°-123°. A single recrystallization generally raised the melting points to 124°-125°, the same as that reported by Vermeulen (2). Larger runs required considerably more time due, at least in part, to our inability to maintain adequate cooling and stirring in the laboratory. Large excesses of both sulfuric and nitric acids were used to facilitate handling of the thick reaction mixture rather than to enhance the reaction. Optimum quantities were found to be one volume of the dimethoxybenzene to six volumes of sulfuric and four volumes of nitric acids. The nitration product tended to float to the top of the acid mixture giving it a consistency much like pancake-batter. If the temperature during the nitration was allowed to rise above 30°, gassing of the mixed acid was appreciable and foaming of the thick mixture became a further problem. Attempts to reduce foaming by increasing the volume of sulfuric acid had an adverse effect probably because the specific gravity of the acid mixture was raised, thereby increasing the tendency of the product to float. The use of both 70% and 90% nitric acid produced good yields but the 90% acid tended to increase gassing and foaming. These problems were apparently minimized when 70% acid was used, the temperature kept below 30°, and stirring was at a moderate rate with a heavy duty stirrer blade the length of which was almost equal to the diameter of the flask.

In plant operations it might be possible to recover the product by direct filtration; in the laboratory, however, drowning in crushed ice was more practical. The drowned mixture should be filtered immediately to eliminate the possibility of hydrolytic cleavage of methoxyl groups. In one run using 735 g of dimethoxybenzene, the drowned mixture stood overnight at room temperature before filtration. The yield was reduced to 77% and the product was yellower than any other obtained during this investigation.

On standing, the filtrate yielded additional solid material of which 2[illegible] g was recovered by filtration. A recrystallized sample of this compound melted at 85°-86° and was identified as 2,4,6-trinitro-3-methoxyphenol by amination to 2,4,6-trinitro-3-aminophenol.

Since even 90% nitric acid contains considerable water, it seemed probable that the exotherm experienced during the addition of nitric acid was due in part to the hydration of the sulfuric acid. Substituting a pre-cooled sulfuric-nitric acid mixture for nitric acid in this step resulted in no appreciable improvement and indicated that this effect was negligable.

Other modifications of the process included dilution of the sulfonation mixture with water prior to nitration, the use of mixed acids in a one step reaction, reversing the order of addition of the acids, and the use of concentrated nitric acid only.

In one reaction using 52.5 g of the dimethoxybenzene and 300 ml of sulfuric acid, 100 ml of water was added to the reaction mixture after sulfonation in an attempt to cut down foaming. On nitration with 200 ml of 90% nitric acid, the primary product was 1,5-dimethoxy-2,4-dinitrobenzene.

When mixed acids were used in an attempted one-step nitration, the reaction temperature was much more difficult to control and rose to 50° during the addition of the acid. The reaction mixture became very dark and resinous, indicating that considerable oxidation had taken place. After a difficult work-up the only product isolated was 1,5-dimethoxy-2,4-dinitrobenzene.

In cases where only nitric acid was used, and where the order of addition of nitric and sulfuric acids was reversed, considerable degradation took place, but the primary product was again 1,5-dimethoxy-2,4-dinitrobenzene. This is somewhat difficult to reconcile with our thinking as to the mechanism of the reaction.

A generally accepted view is that in nitrations of such compounds as phenol, the entry of the first nitro group into the molecule is extremely rapid and exothermic, and that the heat generated in the reaction promotes the oxidative destruction of the molecule. It is also generally held that sulfonation prior to nitration reduces this effect because the sulfonation reaction is less vigorous and the subsequent replacement of the sulfonic acid group is considerably less exothermic than the

replacement of a hydrogen atom. Olsen and Goldstein (7) found that in the preparation of picric acid a mixture of mono- and disulfonic acids was formed in the sulfonation step. In 1,3-dimethoxybenzene, the 2-, 4-, and 6-positions are all doubly activated and the trisulfonic acid might be expected to form under the conditions of the sulfonation reaction (30 min. to 1 hr. at 100°). This is supported by the fact that when nitration was performed without prior sulfonation at a temperature below 60°, and when the order of treatment with nitric and sulfuric acids was reversed at temperatures of 20° or lower, only the dinitro compound could be isolated. This indicates that substitution at the sterically hindered 2-position may take place under the more vigorous conditions of sulfonation reaction and that the sulfonic acid group in this position is replaced by the smaller nitro group more readily than is a hydrogen. However, since the dinitro compound was again obtained by nitration with 90% nitric after first diluting the sulfonation mixture with water, it appears that the trisulfonic acid may never have been formed. It might have been expected that the dinitrosulfonic acid would result under these conditions. This apparent anomaly deserves further investigation.

A small scale run was carried out using 2 g of dimethoxybenzene, 12 ml of 95% sulfuric acid and 8 ml of 70% nitric to determine what would happen should the control of the temperature get out of hand. The nitric acid was added rapidly from a pipette in 2 ml-portions. The temperature rose very rapidly and, by the time 4 ml had entered, it had reached 100°. Further additions of acid resulted in cooling. The reaction mixture was not as clear as under normal conditions but was not resinous. There was no tendency to foam and much of the product had dissolved at the higher temperatures. The yield was 69%.

A summary of nitration reactions is given in Table I.

Amination of 1,3-Dimethoxy-2,4,6-trinitrobenzene: Procedures used in the amination of 2,3,4,6-tetranitroaniline were easily adaptable to 1,3-dimethoxy-2,4,6-trinitrobenzene with good yields.

When a benzene solution of the dimethoxytrinitrobenzene was allowed to stand with methanolic ammonia for 30 min., an excellent quality of 1,3-diamino-2,4,6-trinitrobenzene resulted. The only drawback was the small particle size, which is also the case when DATB is prepared by similar procedures from tetranitroaniline.

The small particle size is probably due to the rapid rate of reaction and the low solubility of the product in the reaction solvent. Efforts were made to retard the rate of reaction by substituting solutions of ammonium acetate and ammonium acetate-acetic acid in methanol for the methanolic ammonia. Variations of these procedures resulted in particle sizes ranging from 20 to 100 microns. An adverse effect on vacuum stability, resulting in values of 4.3 to 7.12 cc of gas per gram per hour at 260°, may have been due to imcomplete removal of acetic acid from the product. It is noteworthy that in a qualitative run a small amount of dimethoxytrinitrobenzene in an acetic acid solution of ammonium **acetate**, heated over night on a steam bath, yielded a product melting at 283°-284° and having a particle size of 500 microns.

EXPERIMENTAL

Nitration of 1,3-Dimethoxybenzene. The optimum procedure for the preparation of 1,3-dimethoxy-2,4,6-trinitrobenzene is described together with two procedures which give good yields of 1,5-dimethoxy-2,4-dinitrobenzene.

1,3-Dimethoxy-2,4,6-trinitrobenzene: A 12 liter 3-neck round bottom flask was fitted with a dropping funnel, thermometer and mechanical stirrer with a heavy-duty Teflon blade whose length was almost equal to the diameter of the flask. The flask was charged with 4200 ml of 95% sulfuric acid, 735 g of 1,3-dimethoxybenzene was added rapidly with stirring and the temperature raised to 90°-100° on a steam bath. The solution turned green and on continued heating, a grey precipitate formed. After 30 min. at 90°-100°, the steam bath was replaced by an efficient ice-salt bath and the temperature lowered to 8°-10°. A volume of 2800 ml of 70% nitric acid was then added through the dropping funnel during the course of 2.5 hours the rate being slow enough to keep the temperature from rising above 30°. The reaction was extremely exothermic and required very efficient cooling. The solution turned red-brown and as the reaction progressed, a tan precipitate formed and tended to float on top of the reaction mixture and to coat the walls of the flask. Since inadequate cooling or stirring at this point

caused considerable foam formation, stirring was at a moderate speed but sufficient to continuously fold the batter below the surface of the solution and to break the cake on the walls. After about 1400 ml of nitric acid had been added, there was no further exotherm and the remainder of the acid was added more rapidly. The mixture was stirred for about 15 min. after the addition of the nitric acid was complete then poured into sufficient crushed ice so that considerable remained unmelted after all of the reaction mixture had been added. As soon as the ice was completely melted, the mixture was filtered through a sintered glass funnel and the filter cake washed thoroughly with cold water. After drying first in air then in the oven at 50°, the crystalline crude product was slightly yellow fine needles, m.p. 121°-123°. Yields were from 83-87%. After crystallization from ethanol, the product melted at 124°-125° and had an impact sensitivity 257 cm (i_{50} = 0.1) on sandpaper (NOL machine, type 12 tools). The crude product was sufficiently pure to be used directly in the amination step.

1,5-Dimethoxy-2,4-dinitrobenzene. Method I: A 100 ml three-neck round bottom flask fitted with a mechanical stirrer, dropping funnel and thermometer was charged with a solution of 5 ml 90% nitric acid in 20 ml acetic anhydride and the temperature lowered to 5° on an ice bath. A solution of 2.1 g 1,3-dimethoxybenzene in 5 ml acetic anhydride was added dropwise with vigorous stirring over a 15 min. period, the rate of addition being slow enough to prevent the temperature from rising above 25°. The reaction was very exothermic and the mixture turned a bright green. After addition was complete, cooling was removed and stirring continued for about three hours, during which time there appeared no further tendency to self heat. Stirring was then discontinued and the reaction mixture allowed to stand at room temperature for 22 hours. The contents of the flask were poured into 200 ml of crushed ice and water, stirred vigorously for a few minutes and filtered through a sintered glass funnel. The filter cake was washed thoroughly with cold water and dried in vacuum desiccator over $CaCl_2$. The yield was 2.83 g (82%) of a wine-colored crystalline solid melting at 142°-143°. On treatment with charcoal and recrystallizing from ethanol the melting point was raised to 154°-155°, and the product was yellowish tan needles. Method II: A 500 ml 3-neck round bottom flask fitted with a mechanical stirrer, a dropping funnel and a thermometer, was charged with 20 ml of 90% nitric acid. With vigorous stirring, 52.5 g of 1,3-dimethoxybenzene was added dropwise, and the temperature maintained at 45°-50° by external cooling. The reaction mixture turned a very dark

red and there was a copious evolution of brown fumes. The addition was complete in about 20 minutes, the temperature was then allowed to rise to 55°-60° for an additional 30 minutes after which self-heating ceased and the solution had turned deep green in color. After an additional 90 minutes without cooling, the temperature had dropped to 35° and the color had changed to deep red. A volume of 200 ml of crushed ice and water was added with stirring whereupon the product coagulated into a gummy mass. The supernatent liquor was decanted off and the gummy residue triturated in 100 ml of hot glacial acetic acid. On cooling in ice, filtering and washing thoroughly with cold water, the residue was dried in the oven at 116°. The yield was 50 g (58%) of tan needles melting at 151°-153°.

Amination of 1,3-Dimethoxy-2,4,6-trinitrobenzene. In this section a standard amination procedure using methanolic ammonia is described together with several experimental procedures designed to give larger particle sizes. The bulk of the dimethoxytrinitrobenzene prepared in this work has been aminated using the improved methods of Shipp, Hall and Hill (9) and will be reported in a subsequent NAVORD Report.

Amination With Amonia: A 200 ml 3-neck round bottom flask was fitted with a mechanical stirrer, a thermometer and a dropping funnel. A volume of 25 ml of absolute methanol was add d to the flask, cooled to 7° and saturated with anhydrous ammonia. Ten grams of 1,3-dimethoxy-2,4,6-trinitrobenzene, was dissolved in 50 ml of warm benzene, the solution filtered and a small amount of insoluble residue on the filter was washed with an additional 10 ml of benzene. The filtrate and washings were cooled to room temperature and added dropwise with cooling and stirring to the methanolic ammonia. The addition required 10 minutes and the reaction temperature was not allowed to rise above 13°. During the addition, the solution immediately becomes red-orange in color and a yellow crystalline solid soon begins to form. Stirring and cooling was continued for an additional 20 minutes after which the yellow solid was collected by filtration and washed with ethanol. After drying first in air then in the vacuum oven at 116°, the product was 8.44 g (96%) of a very fine yellow crystalline material melting at 286°-287° (very slight decomposition). Vacuum stability = 1.7 cc/g/hr. at 260°. Particle size - ca 3 microns.

Amination with Ammonium Acetate: To a solution of ten grams of ammonium acetate in 50 ml of absolute ethanol and 10 ml of

benzene was added in one portion at 70°, fifty grams of 1,3-dimethoxy-2,4,6-trinitrobenzene in 50 ml of absolute ethanol and 30 ml of benzene. A yellow precipitate began to form immediately. The reaction mixture was heated for 15 minutes on the steam bath, cooled to 50°, filtered and the filter cake washed on the funnel first with absolute ethanol then with ether. The glistening yellow crystals were dried first in air then in the vacuum oven at 116°. The yield was 3.79 g (86%), m.p. 283°-284° (dec.). The particle size was 50-60 microns. In the vacuum stability test at 260° the product gave 4.3 cc of gas/g/hr.

Amination with Ammonium Acetate and Acetic Acid: A solution of 50 g of ammonium acetate of 5 ml of glacial acetic in 100 ml of absolute ethanol was brought to a boil on the steam bath. Fifty grams of 1,3-dimethoxy-2,4,6-trinitrobenzene was dissolved in 50 ml of boiling benzene, the solution filtered hot and added to the boiling ammonium acetate-acetic acid solution. A yellow precipitate began to form immediately, and the mixture was allowed to stand on the steam bath at a temperature just below boiling for one hour, cooled to room temperature and allowed to stand over night. The product was collected by filtration and washed, first with absolute ethanol then with ether, and dried in the vacuum oven at 116°. The yield was 3.99 g (91%), m.p. 285°-286°. The particle size was 75-100 microns. In the vacuum stability test at 260° the product gave 7.12 cc of gas/g/hr.

Two modifications of this procedure are summarized in Table II.

Identification of 2,4,6-Trinitro-3-aminophenol: In one preparation of 1,3-dimethoxy-2,4,6-trinitrobenzene, starting with 735 g of 1,3-dimethoxybenzene, the drowned mixture was allowed to stand overnight prior to filtering. A second product precipitated from the filtrate and washings on standing. Sixteen grams of this material melting at 75°-85° was recovered by filtration. On recrystallization, the melting point was raised to 85°-86°.

Two grams of the above product was dissolved in 12 ml of benzene and added slowly with stirring to a solution of 1.5 ml of concentrated ammonium hydroxide in 30 ml of methanol at 50°. The temperature was held at 50° for 20 minutes after addition was complete. Although the color of the solution changed

immediately to orange-yellow, there was no immediate precipitation. On standing overnight at room temperature, there was a small amount of precipitate and the solution was placed in the refrigerator at approximately 5° for an additional 25 hours and filtered. The product was 0.22 g of orange-yellow crystals melting at 253° (dec.). A small amount of the orange-yellow crystals was dissolved in water and the solution acidified with hydrochloric acid. A lemon-yellow precipitate formed immediately. The solution was filtered and the precipitate washed with water. After drying in air, the melting point of the product was 173°-176° and was raised to 175°-176° by recrystallization from ethanol. Mixed melting point with a sample of 2,4,6-trinitro-3-aminophenol (1), 175°-176°.

TABLE I

NITRATION OF 1,3-DIMETHOXYBENZENE (DMB)

Sulfonation				Nitration				Products		
Wt. DMB	Vol. H_2SO_4	Temp. °C	Time (Min)	Vol. HNO_3	Conc. HNO_3	Temp. °C	Time (Min)	Yield	% Yield	Remarks
2.1g	17ml	95-100	105	5ml	96%	5-30	105	3.5g	84	Foaming
2.1g	12ml	90-100	30	8ml	70%	10-100	30	2.9g	69	HNO_3 added rapidly without cooling.
10.5g	60ml	90-95	60	40ml	96%	5-30	80	16.7g	87	
10.5g	60ml	95-100	30	40ml	96%	5-35	30	17.1g	82	Foaming
10.5g	75ml	95-100	30	40ml	96%	5-35	50	17.9g	86	Foaming
10.5g	60ml	98-100	30	40ml	70%	10-30	45	17.2g	83	
10.5g	120ml	90-100	30	14ml	70%	10-30	45	--	--	Foamed badly.
52.2g/a	200ml	10	80	200ml	96%	10-20	30	tar/b		
52.2g	--	--	--	200ml	96%	35-60	120	tar/c		
735g	4200ml	90-100	60	1500ml	70%	5-27	125	1116g	77	Stood overnight in drowning solution.
735g	4200ml	90-95	30	2800ml	70%	10-30	150	1147g	83	Best conditions.
525g	4000ml	80	30	1500ml (1000 H_2SO_4)/d	70%	10-35	105	884g	85	
525g	6000ml	85-90	30	1500ml	70%	10-45	cal50	888g	85	Foamed badly at 45°. Cooled to 25° before continuing.

/a Sulfuric acid added after nitration.
/b Yielded small amount of 1,5-dimethoxy-2,4-dinitrobenzene.
/c Yielded 50 g 1,5-dimethoxy-2,4-dinitrobenzene.
/d Added as mixed acid.

TABLE II

AMINATION OF 1,3-DIMETHOXY-2,4,6-TIRNITROBENZENE (DMTNB)

Wt. DMTNB	Solution A/a	Solution B/a	Reaction Temp.(°C)	Reaction Time	Yield %	m.p. (°C)	Stab. /b	Particle size (μ)
10g	50ml benzene	25ml MeOH sat. with NH_3 at 7°	7-13	30 min.	96	286-7	1.7	3
5g	50ml EtOH 30ml benzene	10g NH_4OAc 50ml EtOH 10ml benzene	60	15 min.	86	283-4	4.3	50-60
5g	50ml benzene	5g NH_4OAc 5ml HOAc 100ml EtOH	75	1 hr.	91	285-6	7.12	75
100g/c	300ml MeOH 300ml benzene 25ml HOAc /d	50g NH_4OAc 250ml MeOH /d	Room temp. /e	over-night	70	---	6.5	50-100
300g	600ml benzene 300ml HOAc	300g NH_4OAc 1500ml MeOH	65/f	over-night	84	---	---	20-60

/a Except as otherwise noted, DMTNB dissolved in solution A and added to solution B.
/b Vacuum stability measured in cc/g/hr. at 260°.
/c Contains 32% water.
/d Solution B added to solutionA.
/e Heated to boiling and filtered hot after standing overnight.
/f Allowed to cool slowly to room temperature and stand overnight.

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